



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07F 9/38		A1	(11) International Publication Number: WO 96/40697 (43) International Publication Date: 19 December 1996 (19.12.96)
<p>(21) International Application Number: PCT/US96/03082</p> <p>(22) International Filing Date: 5 March 1996 (05.03.96)</p> <p>(30) Priority Data: 485,316 7 June 1995 (07.06.95) US</p> <p>(71) Applicant: PASSLEY, Paul, Leonard [US/US]; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).</p> <p>(72) Inventors: DAY, Thomas, McCabe; 439 Magna Carta Drive, Creve Coeur, MO 63141 (US). GILLESPIE, Jane, Laura; 7229 Cornell, University City, MO 63130 (US). KRAMER, Richard, Melvyn; 15238 Kingsman Circle, Chesterfield, MO 63017 (US).</p> <p>(74) Agent: PASSLEY, Paul, Leonard; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).</p>		<p>(81) Designated States: AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, GE, HU, IS, JP, KG, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: PREPARATION OF AMMONIUM GLYPHOSATE VIA A GAS-SOLID REACTION SYSTEM</p> <p>(57) Abstract</p> <p>Solid N-phosphonomethylglycine or glyphosate acid in "wet cake" form is charged to a suitable mixer/reactor. A stoichiometric equivalent of anhydrous ammonia gas is fed to the mixer for direct reaction with the glyphosate acid as it is agitated within the mixer. A water jacket containing circulating water or other suitable heat transfer facilitating means readily known to those in the art is adapted to the mixer and used to remove heat from the reactor produced by the exothermic reaction. The moisture content of the glyphosate wet cake, the design of the mixer including a preferred close tolerance relation between the inner walls of the reactor and its mixing impellers together with the relative location of the ammonia gas inlet in the mixer/reactor and maintenance of a reaction temperature of about 60 °C or below are all important process variables. The ammonium glyphosate thereby produced is a highly sorptive, water-soluble powder suitable for end use as a plant growth regulator or as a herbicide without further processing. Due to the highly sorptive character of the reaction product, however, it is particularly well-suited for further formulation to absorb/adsorb an exceptionally high level of adjuvants such as wetting agents, anti-foaming agents and, in particular, surfactants.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

PREPARATION OF AMMONIUM GLYPHOSATE VIA A GAS-SOLID REACTION SYSTEM

5

BACKGROUND

Field of the Invention

10 This invention relates to a dry, non-clumping herbicidal composition together with a method for making the composition.

More particularly, the present invention relates to a method for making an ammonium glyphosate herbicide by directly reacting ammonia gas with glyphosate acid. The reaction product dissolves readily and completely in water and can be used to prepare highly-loaded, adjuvant-containing dry glyphosate compositions.

20 Description of the Related Art

N-phosphonomethylglycine [HOOCCH₂NH CH₂ PO(OH)₂], which is commonly referred to as glyphosate acid or simply glyphosate, is well known in the art as a highly effective herbicide. It is also known that glyphosate, an organic acid, has relatively low solubility in water. Thus, glyphosate is typically formulated as a water-soluble salt, particularly as the mono-isopropylamine (IPA) salt to kill or control weeds or plants. Glyphosate is sold commercially as an aqueous concentrate in the form of its IPA salt by Monsanto Company of St. Louis, Missouri (U.S.A.) under the registered trademark Roundup®.

Various salts of glyphosate, methods for preparing salts of glyphosate, formulations of glyphosate and methods of use for killing and controlling weeds and plants are disclosed in U.S. Patent Nos. 3,799,758 and 4,405,531 issued to John E. Franz on March 26, 1974 and

September 20, 1983 respectively. Other U.S. Patents which disclose salts of glyphosate include U.S. 4,315,765 issued to George B. Large on February 16, 1982, U.S. 4,507,250 issued to Izak Bakel on March 26, 5 U.S. 4,397,676 issued to Izak Bakel on August 9, 1983, U.S. 4,481,026 issued to Michael P. Prisbylla on November 6, 1984 and U.S. 4,140,513 issued to Erhard J. Prill on February 20, 1979. All of the foregoing 10 patents, in their entireties, are herein incorporated by reference.

Roundup® brand herbicide is sold as a water-soluble liquid concentrate. However, efforts have recently been made in the art to develop a water-soluble dry/solid glyphosate formulation which has the equivalent efficacy 15 of Roundup®.

Conventional reasons underlying these efforts have been desired cost savings in connection with the packaging, shipment and storage of a solid formulation versus a liquid. As can be appreciated, aqueous 20 concentrates include a significant amount of solvent that adds to the size and weight of packaging containers and increases costs associated with post-manufacture delivery of the product to market.

A less readily apparent benefit also resides in the 25 advantage of making a water-soluble, dry glyphosate. Namely, a granular formulation is believed to provide superior handling characteristics (i.e. controlled spillage) and is expected to be substantially lighter and less awkward to transport (and often hand carry) 30 thereby making the product better suited for use in remote geographic locations.

Making a granular glyphosate formulation, however, entails overcoming inherent disadvantages relating principally to the increased production cost and 35 comparative complexity of compounding a solid product from a combination of gaseous and solid reactants rather

than making a product in solution from the same reactants.

Several methods of making a solid water-soluble glyphosate salt-containing composition are known. For 5 example, in U.S. Patent No. 5,047,079 which issued on September 10, 1991 to Djafar, there is disclosed a method for preparing a phytotoxic composition comprising admixing isopropylamine with a molten surfactant to form a matrix, the surfactant being a solid at ambient 10 temperatures.

In U.S. Patent No. 5,070,197 which issued on December 3, 1991 to Chin, et. al. an extrusion method is disclosed in which a Bronsted acid, N-phosphonomethyl glycine for example, is intimately admixed with sodium 15 hydroxide in an extruder to produce a granular extrudate having a residual moisture content of no greater than 10%. Another method involving the production of a dry sodium glyphosate composition, albeit not involving extrusion, is disclosed in PCT application Publication 20 No. WO 87/04595.

In U.S. Patent No. 5,266,553 which issued on November 30, 1993 to Champion, et. al. there is disclosed a method for preparing a dry, water-soluble salt of bentazon or of an herbicide containing a 25 carboxylic acid functionality which involves repeated treatments of the salt with a neutralizing base selected from the group consisting of ammonia, an alkylamine, a hydroxyalkylamine, an alkaline salt of an alkali metal and combinations thereof.

30 In French Patent Publication No. 2.692.439 which was filed on May 19, 1993 and is assigned to Productos Osa SACIFIA, there is generally described a phytotoxic preparation comprising the monoammonium salt of N-phosphonomethylglycine as a powder or granule in 35 combination with a wetting agent, surfactant and/or a pulverulent additive. As exemplified in the reference,

the monoammonium salt is derived from reacting glyphosate acid with ammonium carbonate.

U.S. Patent No. 5,324,708 which issued on June 28, 1994 to Moreno, et. al. discloses a composition and 5 related methods for preparing and using a non-hygroscopic monoammonium glyphosate salt such as the mono-isopropylammonium salt of N-(phosphono-methyl)-glycine and the mono-isopropylammonium salt of (3-amino-3-carboxypropyl)-methane phosphonic acid in dry powder 10 form [sic].

In PCT application Publication No. WO 94/10844, published on May 26, 1994, a dry glyphosate composition is disclosed in which N-phosphonomethyl glycine is admixed with, inter alia, an inorganic or organic, non-15 caustic base material such as diammonium phosphate or a basic guanidine salt such as guanidinium acetate.

EPO application Publication No. 0 394 211 which was published on October 24, 1990, discloses an invention comprising a dry pesticidal composition and related 20 methods of use and production. More particularly, the invention relates to the enhanced solubility of the composition as achieved by the addition of an effective amount of an organosilicone block copolymer or a fluorocarbon wetting agent.

25 In EPO application Publication No. WO 90/07275 which was published on July 12, 1990, there is disclosed an invention by which granular, water-soluble glyphosate compositions are made as by admixing, pan granulation, drying, spraying and extrusion.

30 In PCT application Publication No. WO 92/12637, which was published on August 6, 1992, there is disclosed an invention relating to a dry, water soluble glyphosate including a composition comprising substantially nonreacted glyphosate, an acid acceptor 35 such as sodium acetate and a liquid or solid surfactant.

All of the foregoing patents and publications are herein incorporated by reference.

The art indicates that considerable effort has been directed toward formulating compositions and related methods for making and using dry glyphosates. However, none of the above-identified references disclose a

5 direct and practical method for producing a dry, water-dispersible, water-soluble and appreciably non-hygroscopic ammonium glyphosate composition which is capable of absorbing/adsorbing an exceptionally high level of adjuvants by reacting solid N-

10 phosphonomethylglycine with relatively inexpensive and plentiful ammonia gas.

Thus, a need unsatisfied by known technology exists within the art for the present invention which accomplishes these and other objectives.

15

Summary Of The Invention

The unresolved needs of the art are satisfied by the present invention which provides an ammonium

20 glyphosate dry herbicide composition and novel method for its production whereby the disadvantages associated with known dry compositions and related methods, as discussed, are overcome through heretofore unknown and undisclosed limitations.

25 In accordance with the present invention glyphosate acid in "wet cake" form having a moisture content of up to approximately 20 wt.% (i.e. weight loss on drying or LOD) is charged to a suitable reactor system such as a conventional mixing apparatus. As the mixer agitates

30 the wet cake, it is neutralized by a stoichiometric equivalent of anhydrous ammonia gas which is fed directly to the mixer for reaction with the wet cake.

Because the reaction is exothermic, it is desirable to employ a means for facilitating heat transfer from

35 the reactor system such as a fitted water jacket about the mixer or other means conventionally known in the art in order to dissipate heat produced by the reaction and

thereby partially control the temperature of the reaction. Additionally in this regard, the configuration of the mixer/reaction vessel and, particularly self-cleaning features and the placement of 5 the ammonia gas inlet have proven to be important process variables. Also, the internal reactor temperature is monitored and controlled such that a temperature of about 60° C is not exceeded.

Further, and in combination, the relative moisture 10 content of the wet cake and the rate at which the ammonia gas is added to the reaction, among other things, have also been found to be factors that influence the manageability of the reaction mass. Thus, an important aspect of the present invention relates to 15 the manner in which all of these variables are managed in order that the heat balance can be controlled and a desirable product thereby produced.

The ammonium glyphosate composition produced in accordance with the process of the present invention is 20 in the form of a powder which is suitable for end use as a plant growth regulator and/or a herbicide.

Perhaps more importantly, however, the powdered reaction mass/product due to its highly sorptive character is capable of being further formulated to 25 absorb/adsorb an exceptionally high level of adjuvants such as wetting agents, anti-foaming agents and, particularly, surfactants. Thus, when so formulated, a very useful and highly desirable adjuvant-loaded product is formed which is every bit as good and effective as 30 comparable products obtained by prior art processes which require more expensive starting materials.

Optionally, the powdered reaction product or the adjuvant-loaded product may each be granulated to provide a free-flowing (i.e. non-caking), substantially 35 dust-free and water soluble ammonium glyphosate herbicide and/or plant growth regulator.

Still further optional procedures may be carried out using the powdered reaction product. For example, the powder may be further ground and/or dried prefatory to packaging.

5 Significant advantages achieved by the present invention reside in its relative simplicity and comparatively low cost of the reactants. Furthermore, the process of the present invention is very efficient. That is, because the ammonia gas is reacted directly
10 with the solid glyphosate acid to produce a powder, the significant problem of isolating the ammonium glyphosate in solid form from a solution is eliminated.

Detailed Description of the Invention

15 The present invention relates to a novel method for reacting N-phosphonomethylglycine (glyphosate acid) with anhydrous ammonia gas to produce high quality ammonium glyphosate powder, a key raw material used in the production of granular and/or surfactant-loaded dry
20 glyphosate compositions.

Until now, an effective and practical method for producing dry ammonium glyphosate powder capable of being further formulated to absorb/adsorb an exceptionally high level of adjuvants by reacting
25 glyphosate acid and ammonia gas has not been known.

Instead, various alternate and less advantageous methods have been developed by which ammonium glyphosate as well as alkali metal glyphosates such as sodium glyphosate have been made in dry, powder form. For
30 example, sodium glyphosate has been produced by reacting glyphosate acid with sodium acetate or by extruding the acid with sodium hydroxide as described above in PCT application Publication No. WO 92/12637 and U.S. Patent No. 5,070,197 respectively.

35 Sodium glyphosate granules and powders have, until now, provided a satisfactory dry glyphosate composition. However, when compared to ammonium glyphosate

compositions, the sodium alkali metal is many orders more hygroscopic meaning it is not as resistant against ambient humidity. Thus, the sodium alkali metal glyphosate is considered more difficult and more 5 expensive to process as a dry composition and, once formed as such, these compositions have a greater tendency to agglomerate which results in undesirable "caking" of the finished material.

Also, due to the relative molecular weights of 10 ammonia and sodium, sodium glyphosate salt compositions have a lower concentration of the active glyphosate than their counterpart ammonium glyphosate salt compositions. In addition, the per pound cost of sodium cation is much more expensive than the cost of obtaining an equivalent 15 amount of the ammonium cation. The comparative disadvantages of sodium glyphosate compositions are, thus, apparent.

As previously noted, certain solid/solid reaction methods are also known for making dry ammonium 20 glyphosate. Reacting ammonium bicarbonate with glyphosate acid, for example, as described above in French Publication No. 2.692.439 is believed to yield a dry ammonium glyphosate composition.

The invention disclosed herein, however, 25 constitutes an advance in the art of making dry ammonium glyphosate notwithstanding known methods utilizing ammonium bicarbonate.

For example, in practicing the present invention which involves reacting anhydrous ammonia gas with solid 30 N-phosphono-methylglycine, it has been observed that the per pound cost of ammonium cation derived from ammonium bicarbonate is several times more expensive than the per pound cost of obtaining an equivalent amount of the same cation from ammonia gas.

35 In the large-scale commercial production of ammonium glyphosate, a cost differential such as this might alone militate in favor of an effective method, such as that

disclosed herein, for producing a solid ammonium glyphosate using anhydrous ammonia gas as the source of ammonium cation.

As used herein the terms "solid" and/or "dry" mean 5 the physical state in which the formulation has a specific shape and volume and resists deformation. The solid may take the form of pellets, flakes, granules, powder or the like. Further, it will be understood that the solid formulation may subsequently be dissolved in a 10 suitable diluent, usually and preferably water, and applied to the locus where plant regulation or eradication is desired as by spraying or other conventional means.

From a technical perspective, very little is known 15 about the use of ammonia gas in processes such as that disclosed herein. When this is considered in combination with the safe, cost-effective and technically simple ammonia gas process of the present invention the results obtained thereby are not to be 20 expected.

The reaction of ammonia gas with glyphosate acid to produce ammonium glyphosate is, perhaps, the least expensive and most direct chemical approach possible. This is because the reaction involves the most 25 fundamental reactants including plentiful and comparatively inexpensive ammonia gas which is reacted with glyphosate acid in a simple addition reaction. Moreover, because the chemistry of the reaction is so simple, no by-products such as water are produced which 30 would complicate the reaction and require removal such as is the case where ammonium hydroxide is reacted with glyphosate acid. Despite the obvious advantages of the process of the present invention, however, it has been observed that the reaction that occurs between N- 35 phosphonomethylglycine and anhydrous ammonia gas is, typically, highly exothermic. Thus, in practicing the present invention, a major factor to be contended with

relates to heat transfer away from the reaction vessel.

Where the heat transfer in the reaction system is low and unmanaged, the reaction product thereby formed is often an undesirable "dough-like" cohesive mass and/or

5 "glassy" solid reaction mass which may make it difficult to continue the reaction. Furthermore, such a product is not suitable for use as a finished product and is incompatible with conventional formulation equipment used in further processing.

10 Because heat transfer plays such an important role in the reaction of ammonia gas with glyphosate acid, it is very important that the reactor vessel in which the reaction takes place is designed in such a way as to ensure a high degree of unencumbered heat transfer away

15 from the reactor.

In this regard, it is very desirable that the mixing apparatus/reactor have desirably close tolerances between the edges of the mixing components (i.e. impellers) and the internal walls of the reactor. This

20 is because, as the reaction proceeds, there is a tendency for reaction mass/product to adhere to the interior walls of the reation vessel. Where the tolerances between the impellers and the walls is not sufficiently close as to permit the impellers to

25 continuously scrape the product from the walls, the reaction mass/product forms a glassy solid lining along the inner walls of the reactor.

Even when such glassy product is formed in only a thin layer along the reactor walls, it can act as an

30 insulating thermal barrier inside the reactor which reduces heat transfer and frustrates the role of heat transfer equipment already in place.

This condition and the glassy solid product formed in connection therewith are wholly distinct from the

35 process of the present invention which allows for the formation of a highly desirable free-flowing powdered

product which is particularly well-suited to be further formulated.

Thus, adherence to the novel process herein disclosed and the manner and extent to which the 5 reaction between the glyphosate acid and the anhydrous ammonia gas is controlled in accordance with the process, are very significant in ensuring the creation of a solid, free-flowing (i.e. non-caking) and water soluble/dispersible ammonium glyphosate product which is 10 characteristic of the present invention.

In accordance with the process of the present invention, the reactants are combined in such a manner as to ensure substantially uniform dispersion of the ammonia gas within the glyphosate wet cake. The 15 temperature of the reaction is carefully monitored and controlled by various process variables including the rate of ammonia gas addition and by employing suitable heat transfer means widely known to those skilled in the art such as by adapting a circulating water jacket about 20 the reactor and/or the reactor impellers in order that a free-flowing, readily handleable powdered product is generated. Adherence to the process of the present invention not only permits processing in conventional equipment or slightly modified versions thereof but also 25 produces an ammonium glyphosate powder that can be used to make dry glyphosate products highly-loaded with adjuvants.

The inventors have determined that, among other things, the relative moisture content in the glyphosate 30 acid starting material is an important aspect of the invention.

The amount of ammonia gas required in order to practice the invention is equivalent to that amount which is required to achieve approximately 95 - 105% 35 neutralization of the acid which can be determined by conventional analytical methods readily known to those skilled in the art such as by pH measurement.

In accordance with the process of the present invention an amount of glyphosate acid wet cake having a moisture content of up to about 12 wt.% and not less than about 3 wt.% is charged to a suitable reactor 5 system such as a conventional blender or mixer and preferably one having internal blending or mixing impellers designed in close tolerance to the internal walls of the reactor/mixer. A glyphosate composition having a higher moisture content may also be used in the 10 process of the invention although it is preferred that such a composition first be dried to reduce the moisture content to within the preferred range.

Optionally, a pre-determined quantity of sodium sulfite may be added to the glyphosate acid to prevent 15 the possible formation of nitrosamines. Although the addition of sodium sulfite is not necessary to practice the invention and does not affect the reaction between the glyphosate acid and the ammonia gas, certain governmental regulations require that nitrosamine levels 20 in agricultural products of this nature be below 1 ppm. Experience has shown that, when added, the effective range of sodium sulfite to be added as ensurance against the presence of unacceptable levels of nitrosamines is between about 0.2 and about 1.0 wt.% of the dried, 25 finished product.

Once the glyphosate wet cake and sodium sulfite, 30 optionally, have been charged to the reactor/mixer, one stoichiometric equivalent of anhydrous ammonia gas is then fed directly to the reactor while the wet cake is being agitated and blended. Because the reaction is exothermic, suitable heat transfer means such as a 35 circulating cold water jacket or other means readily known to those skilled in the art should be adapted to the reactor system in order to facilitate heat transfer and thereby provide some control over the temperature of the reaction within the reactor.

Throughout the step of ammonia gas addition various process variables, including ammonia gas addition rate and reaction temperature, are controlled such that a free-flowing, readily handleable and highly sorptive 5 powdery ammonium glyphosate product is formed.

As can be appreciated, the novel process can be readily practiced using conventional equipment which is preferably designed to be substantially self-cleaning. Also, however, other equipment not so designed may also 10 be employed in which case some measure, such as perhaps intermittent manual scraping for example, must be incorporated in conjunction with the process in order to keep the heat transfer surfaces of the reactor clean and free from product build-up. Unless this measure is 15 provided for, the reaction mass/product, with continued processing, forms a thermal insulating layer on the inner walls of the reactor which frustrates heat transfer and which may lead to an uncontrolled reaction temperature resulting in overheating of the product and 20 thereby destroying its desirable characteristics.

The inventors have discovered that the manner in which the ammonia gas is introduced to the blender for reaction with the glyphosate acid is a very significant aspect of the invention. In accordance with the 25 invention, the ammonia gas should be introduced to the reactor in such a manner as to ensure substantially thorough and uniform dispersion of the gas with the glyphosate acid. This precept is carried out in the invention when the inlet port or ports through which the 30 ammonia gas is introduced into the reactor is/are positioned in such a manner as to ensure that sufficient quantities of the acid are being contacted with the gas, as the acid is being agitated and the gas is being introduced, to form a reaction mass/product which is the 35 result of a reaction in which ammonia gas has been uniformly reacted with the glyphosate acid. The improper placement of the ammonia gas inlet(s) will

likely result in fouling of the inlet(s) and/or the formation of an undesirable "dough-like" cohesive mass or solid glassy product. For example, where an inlet only permits the ammonia gas to react with a small, 5 localized quantity of the glyphosate acid within the reactor, it is likely that a "hot spot" will be formed whereby the localized reaction mass overheats due to the build-up of excessive localized heat from the exothermic reaction. This phenomenon could not only contaminate 10 the entire product being produced at the time, but also possibly clog the gas inlet(s) thereby raising the possibility of physical damage to the processing equipment and creating the possibility of an ammonia gas escape.

15 In addition to the other process variables identified, it has been determined that the temperature of the reaction mass is, at least partially, a function of the rate of ammonia gas addition to the reaction. In this regard it has been determined that it is desirable 20 to maintain a reaction mass temperature of about 60° C or less in order to maximize the production of a valuable product.

Under the process conditions disclosed and described, the direct reaction of ammonia gas with 25 glyphosate acid results in the production of a highly desirable ammonium glyphosate product capable of being further formulated to absorb/adsorb an exceptionally high level of adjuvants. These conditions which include the configuration of the mixer/reactor, the relative 30 moisture content of the starting glyphosate acid, the rate and manner in which ammonia gas is added to the reaction and various methods for facilitating heat transfer away from the reactor vessel are all designed to control the temperature of the reaction mass which, 35 in turn, assures that a manageable powdered product suitable for further processing is obtained.

A number of process variables falling outside the scope of the requirements of the present invention will adversely affect the advantages achieved by the process of the present invention. For example, if the 5 temperature in the reaction mass is allowed to rise above about 60° C, the quality of the reaction mass/product can be substantially deteriorated.

10 The following example illustrates production of the composition of the invention in accordance with the process described herein. All percentages are based upon weight, unless otherwise clearly indicated.

EXAMPLE 1

15

In a plant-scale reactor system comprised of a 300 Liter stainless steel horizontally mixer/reactor fitted with cross-flow mixing tools, a high-speed chopper and a water jacket containing circulating cold water, 94.6 20 lbs. of standard grade N-phosphonomethylglycine "wet cake" having an assayed moisture content of about 7.4 wt.% was charged to the mixer/reactor where it was immediately mixed.

Once all of the wet cake was deposited in the 25 mixer, 0.4 lbs. of solid anhydrous sodium sulfite was also charged, optionally, to the mixer and admixed with the wet cake.

The admixture of wet cake and sodium sulfite was then circulated within the mixer/reactor for a time 30 sufficient to obtain a substantially uniform mixture.

Through an inlet disposed centrally within the mixer/reactor whereat the largest volume of the admixture could be contacted, 8.65 lbs of anhydrous ammonia gas was then introduced into the reactor at a 35 rate of about 0.2 lbs./min. and reacted directly with the glyphosate acid admixture. A temperature probe was positioned within the reactor in order to monitor the

temperature of the exothermic acid-base reaction that ensued. A reaction mass temperature not exceeding 60° C was maintained in part due to the rate of ammonia gas addition established in connection therewith.

5 Once the final product was obtained, it was dried in a vacuum oven at 50° C under vacuum. The dried product was then ground in a hammer mill fitted with a 40 mesh screen. The resulting finished product exhibited a moisture content of no greater than 1.0

10 wt.-%.

From the original reactants which included 94.6 lbs. of glyphosate acid (i.e. "wet cake" containing 7.4% LOD) and 8.65 lbs. of anhydrous ammonia gas, a theoretical product yield of 97 lbs. of dry, powdered

15 ammonium glyphosate having a residual moisture content of approximately 1.0 wt.% can be obtained.

The product obtained in connection with the foregoing example has demonstrated excellent storage and stability characteristics. In fact when stored

20 properly, as for example in sealed polyethylene bags, the product has proven not to degrade or cake after six months of actual warehousing.

25 As discussed in some detail above, the powdered reaction mass/product produced in accordance with the novel process of this invention is particularly well adapted to be further formulated to absorb/adsorb high levels of adjuvants.

30 In combination, the relative simplicity of the present invention, its ability to be practiced in conventional or slightly modified conventional equipment and the comparatively low cost of the ammonium cation furnished by the ammonia gas deem very significant the

35 capacity of the powdered reaction mass/product to absorb/adsorb high levels of adjuvants.

While the choice of a particular adjuvant or combination of adjuvants will be easily made by those ordinarily skilled in the art without undue experimentation, Example 2 presented below illustrates 5 the exceptional sorptive capacity of the powdered reaction mass/product when loaded with surfactant.

EXAMPLE 2

10

The powdered reaction mass/product formed by the process as illustrated in Example 1 can be used to make a dry formulation of ammonium glyphosate containing a high level of surfactant of at least up to about 20 15 wt.%.

To make such a highly loaded product, 16 kilograms of the powdered reaction mass/product is blended with 4 kilograms of a polyoxyethylene alkylamine surfactant and 1.4 kilograms of water in a jacketed batch kneader, such 20 as a Fuji Paudal, for approximately 10 minutes with water at a temperature of about 80° C circulating in the jacket. The dough that is formed is then extruded, as for example in a Fuji Paudal twin screw extruder, fitted with screens having approximately 1 mm. diameter 25 borings. The extrudate obtained consisted of discrete, "spaghetti-like" short noodles which did not stick together and which were easily and conveniently dried, such as for example in a Fitz-Aire fluid bed dryer, without formation of undesirable lumping.

30 The dry ammonium glyphosate herbicide of this invention is effective when subsequently dissolved or dispersed in a suitable diluent, preferably water, and applied to the locus of the target plant by spraying or other conventional means.

CLAIMS

WHAT IS CLAIMED IS:

5 1. A method for preparing a phytoactive ammonium glyphosate comprising introducing anhydrous ammonia gas to a glyphosate acid medium to cause a reaction therebetween in a manner such that said gas is uniformly dispersed with said acid and such that the transfer of
10 heat away from said reaction is optimalized.

2. The method of Claim 1 wherein said glyphosate acid has a moisture content of up to approximately 12 wt.%.

15 3. The method of Claim 1 wherein said glyphosate acid may have a moisture content of up to approximately 20 wt.% but, in such case, is first dried to reduce said moisture content to up to about 12 wt.% prior to being
20 reacted with said ammonia gas.

4. The method of Claim 1 wherein said glyphosate acid has a moisture content of no less than approximately 3 wt.%.

25 5. The method of Claim 1 wherein said glyphosate acid has a moisture content of up to approximately 12 wt.% but not less than approximately 3 wt.%.

30 6. The method of Claim 1 wherein said reaction is carried out in a substantially self-cleaning conventional mixer.

35 7. The method of Claim 1 wherein the temperature of the reaction mass/product generated by said reaction is maintained at approximately 60° C and controlled, at

least in part, by adjusting the rate at which said ammonia gas is reacted with said acid.

8. The method of Claim 1 wherein said reaction is
5 carried out in a substantially self-cleaning
mixer/reactor and wherein the temperature of the
reaction mass/product generated by said reaction is
maintained at approximately 60° C and controlled, at
least in part, by ensuring that the interior walls of
10 said reactor are free from product build-up.

9. The method of Claim 1 wherein said reaction is
carried out in a substantially self-cleaning
mixer/reactor and wherein the temperature of the
15 reaction mass/product generated by said reaction is
maintained at approximately 60° C and controlled, at
least in part, by a combination of two or more process
variables which include adapting a circulating water
jacket or other conventionally known means for
20 facilitating heat transfer to said mixer/reactor,
adjusting the rate at which said ammonia gas is reacted
with said acid to maintain said temperature and ensuring
that the interior walls of said reactor are free from
product build-up.

25

10. The method of Claim 1 wherein said ammonia gas
and said acid are reacted in substantially equivalent
stoichiometric amounts.

30 11. The method of Claim 1 wherein the required
amount of said ammonia gas is equivalent to an amount
sufficient to neutralize approximately 95 to about 105%
of said acid.

35 12. The method of Claim 6 wherein said glyphosate
acid has a moisture content of up to approximately 12
wt.% but not less than approximately 3 wt.% and wherein

the temperature of the reaction mass/product generated by said reaction is maintained at approximately 60° C and controlled, at least in part, by adjusting the rate at which said ammonia gas is reacted with said acid.

5

13. The method of Claim 6 wherein said glyphosate acid has a moisture content of up to approximately 12 wt.% but not less than approximately 3 wt.% and wherein the temperature of the reaction mass/product generated by said reaction is maintained at approximately 60° C and controlled, at least in part, by ensuring that the interior walls of said reactor are free from product build-up.

10

14. The method of Claim 9 wherein said combination of process variables further includes adapting to said mixer/reactor a circulating water jacket or other conventionally known means for facilitating heat transfer.

15

15. A method for preparing a dry ammonium glyphosate capable of being highly loaded with adjuvants comprising the steps of:

(a) charging to a substantially self-cleaning mixer/reactor a quantity of glyphosate acid wet cake;

25 (b) introducing a quantity of anhydrous ammonia gas to said reactor to cause a reaction between said gas and said acid; and

(c) controlling the temperature of the reaction mass/product generated by said reaction in a manner such as to maintain said temperature at a desired level of up to about 60° C.

30

35 16. The method of Claim 15 wherein said glyphosate acid wet cake has a moisture content of at least about 3 wt.% and up to about 12 wt.% and wherein said gas and

said acid are reacted in substantially equivalent stoichiometric amounts.

17. The method of Claim 15 wherein the step of
5 controlling said temperature of said reaction
mass/product further includes adjusting the rate at
which said ammonia gas is introduced to maintain said
temperature at said desired level.

10 18. The method of Claim 15 wherein the step of
controlling said temperature of said reaction
mass/product further includes adapting a circulating
water jacket or other conventionally known means for
facilitating heat transfer to said mixer/reactor.

15

19. The method of Claim 15 wherein the step of
controlling said temperature of said reaction
mass/product further includes, in any combination of two
or more, adapting a circulating water jacket or other
20 conventionally known means for facilitating heat
transfer to said blender/reactor, adjusting the rate at
which said ammonia gas is introduced to maintain said
temperature at said desired level and/or by ensuring
that the interior walls of said reactor are free from
25 product build-up.

20. The method of Claim 15 wherein the step of
introducing said ammonia gas further includes means for
ensuring that said gas is uniformly dispersed with said
30 acid at the time of said reaction.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/03082

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F9/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 256 608 (STAUFFER CHEMICAL CO) 24 February 1988 cited in the application see the whole document ---	1-20
A	EP,A,0 238 240 (UNIROYAL CHEM CO INC) 23 September 1987 cited in the application see the whole document ---	1-20
A	US,A,5 266 553 (CHAMPION JAMES K ET AL) 30 November 1993 cited in the application see the whole document ---	1-20

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 July 1996	22.07.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Beslier, L

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 96/03082	
---	--

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 692 439 (OSA SACIFIA PROD) 24 December 1993 cited in the application see the whole document ---	1-20
A	WO,A,92 18513 (ALKALOIDA VEGYESZETI GYAR) 29 October 1992 cited in the application see the whole document ---	1-20
A	EP,A,0 582 561 (MONSANTO CO) 9 February 1994 see the whole document ---	1-20
A	WO,A,90 07275 (MONSANTO CO) 12 July 1990 cited in the application see the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/03082

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0256608	24-02-88	CA-A-	1309266	27-10-92
		DE-A-	3778089	14-05-92
		DK-B-	170456	11-09-95
		JP-B-	8025849	13-03-96
		JP-A-	63051307	04-03-88
		RU-C-	2038790	09-07-95
		US-A-	5047079	10-09-91
<hr/>				
EP-A-0238240	23-09-87	AU-B-	602137	04-10-90
		AU-B-	7019587	24-09-87
		CA-A-	1297696	24-03-92
		DE-D-	3787107	30-09-93
		DE-T-	3787107	20-01-94
		ES-T-	2058106	01-11-94
		JP-C-	1714157	27-11-92
		JP-B-	4001721	14-01-92
		JP-A-	62230701	09-10-87
		US-A-	5070197	03-12-91
		ZA-A-	8701571	24-08-87
<hr/>				
US-A-5266553	30-11-93	NONE		
<hr/>				
FR-A-2692439	24-12-93	BR-A-	9300433	08-09-93
<hr/>				
WO-A-9218513	29-10-92	HU-A-	72428	29-04-96
		HU-A-	72429	29-04-96
		HU-A-	72427	29-04-96
		AT-T-	139236	15-06-96
		AU-B-	653226	22-09-94
		AU-B-	1653592	17-11-92
		BG-A-	97162	30-06-94
		BR-A-	9205234	27-07-93
		CA-A-	2084663	17-10-92
		EP-A-	0537318	21-04-93
		JP-T-	6500339	13-01-94
		PL-A-	297358	10-01-94
		SK-A-	366992	10-05-95
		US-A-	5410075	25-04-95
		US-A-	5324708	28-06-94
		LT-A,B	129	25-09-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/03082

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0582561	09-02-94	AU-B-	4432493	03-02-94
		CA-A-	2101669	01-02-94
		JP-A-	6256121	13-09-94
		NZ-A-	248289	24-02-95
<hr/>				
WO-A-9007275	12-07-90	AT-T-	139670	15-07-96
		AU-B-	635514	25-03-93
		AU-B-	4833390	01-08-90
		CA-A-	2006816	30-06-90
		EP-A-	0378985	25-07-90
		EP-A-	0452366	23-10-91
		JP-T-	4502618	14-05-92